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Metastability of the midgap level *EL*2 in GaAs: Relationship with the As antisite defect

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We find that the rate of the photoinduced transition of the GaAs midgap level *EL*2 to its metastable state increases as its occupation increases. High-resolution optical spectra of this transition exhibit a sharp peak very similar to the no-phonon line of the intracenter absorption of the As antisite defect. These findings show that the transition to the metastable state is initiated from the ground state $^1A_1$, and it is finalized via the excited state $^1T_2$ of the neutral As antisite defect. They thus provide a new basis for the critical assessment of the *EL*2 metastability models and further confirmation of the association of *EL*2 with the isolated As antisite defect.

The midgap donor *EL*2 is a dominant deep level in GaAs crystals grown from the melt or from the vapor phase. It originates in native defects and plays the major role in the compensation of "undoped" semi-insulating GaAs utilized for integrated circuits. This role provided the motivation for very intensive investigations of *EL*2 which have recently been focused on two inter-related problems: (a) the relationship between *EL*2 and the arsenic antisite defect,[1-4] and (b) the understanding of the very unusual optical properties of *EL*2 (at reduced temperatures, $T \lesssim 140$ K), which are manifested as persistent optical bleaching,[5,6] photocapacitance quenching,[7-9] and luminescence fatigue.[10,11] These properties clearly relate to the dual nature of the *EL*2 center characterized by two states: a normal state and a metastable state.

In this Rapid Communication we report new experimental results on the kinetics of the photoinduced transition of *EL*2 from the normal to the metastable state as a function of the occupancy of the *EL*2 and as a function of the photon energy. These results relate the *EL*2 transition to the metastable state with the fine structure of intracenter transition in the As antisite defect in its neutral state.

The present study was carried out on a series of GaAs crystals especially grown to ensure the presence of only one midgap level *EL*2, since bulk GaAs crystals can, in general, contain other midgap levels with similar activation energy to those of *EL*2 (referred to as "*EL*2 family").[12-15] Oxygen impurity[13] and/or excessive thermal stress[16] have been suggested as causes for such levels. Our GaAs crystals were grown by the horizontal Bridgman method under conditions of negligible thermal stress and without oxygen doping.

The *EL*2 transition to the metastable state was studied using photocapacitance transient measurements. Semitransparent Au Schottky diodes were evaporated on *n*-type GaAs samples with a free-electron concentration of about 5×10^{16} cm^{-3} at 300 K. The diodes were placed on a cold finger of a variable-temperature cryostat and the capacitance changes were monitored with a 1 MHz capacitance bridge. The samples remained conducting even at the lowest temperature employed in this study, about 8 K.

The transition of *EL*2 into the metastable state leads to a characteristic photocapacitance transient of a reverse biased diode illuminated with photons with energy ranging from 1 to 1.3 eV. As shown in Fig. 1(a), this photocapacitance transient consists of two distinct stages: an initial fast increase of capacitance caused by photoionization of *EL*2 and a subsequent slow decrease of capacitance which corresponds to the *EL*2 transition to the metastable state. Since *EL*2 is partially ionized within the depleted region, after the fast photoionization stage it is not possible to decide from the photocapacitance transient itself whether the transition to the metastable state originates in the occupied (neutral) or in the ionized (positively charged) *EL*2.

The analysis of the photocapacitance was carried out using the capacitance changes ΔC_1 and $\Delta C_2(t)$, shown in Fig. 1(a), and the corresponding *EL*2 parameters [shown in Fig.

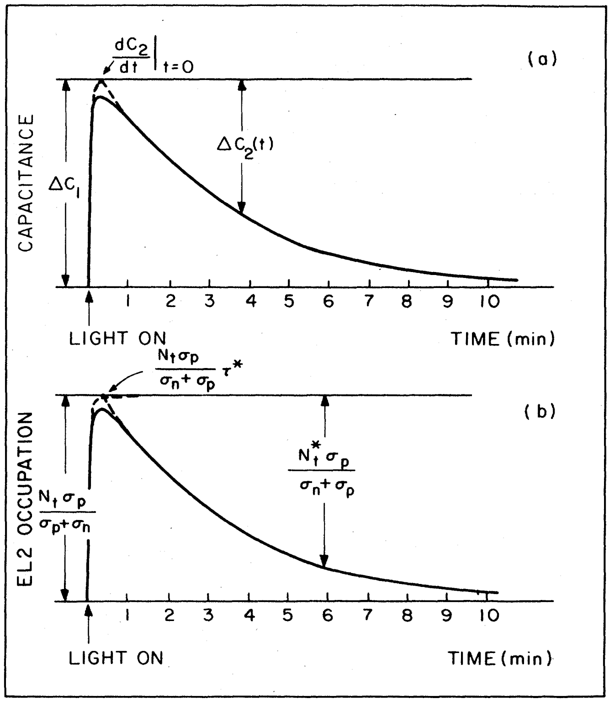

FIG. 1. Photocapacitance transients showing transition to the metastable state described in terms of (a) capacitance changes, and (b) *EL*2 occupancy. (See text.)

1(b)]: N_t, N_t^n, and N_t^*, i.e., the total *EL*2 concentration, the concentration of *EL*2 in the normal state, and the concentration of *EL*2 in the metastable state, respectively; the concentration of occupied *EL*2 in the normal state is designated as n_t, the photoionization cross sections of the normal state for electrons and holes are designated as σ_n^I and σ_p^I, respectively, and the time constant of the transition to the metastable state as τ^*.

The rate of the transition can be determined from the initial slope of the capacitance decrease $dC_2/dt|_{t\to 0}$. For *EL*2 concentrations, small compared to the net concentration of shallow ionized centers, the ratio N_t^*/N_t becomes equal to $1-\Delta C_2/\Delta C_1$.

The dependence of N_t^*/N_t on the illumination time is shown in Fig. 2 for two distinct conditions: (a) the diode is under reverse bias (-5 V) during illumination (standard measurement); and (b) the diode is biased in a forward direction during illumination. It is seen from Fig. 2 that in case (b) the transition is about twice as fast as in case (a). All experimental parameters other than bias voltage (i.e., photon energy, photon flux, elapsed illumination time and temperature, $T=8$ K) were kept exactly the same. Also, in both cases *EL*2 was brought to a normal state by raising the temperature up to 70 K, with a "forward bias" prior to measurements at the low temperatures $T=8$ K.

The results of Fig. 2 can be explained considering that the transition to the metastable state is realized from occupied *EL*2 only. For forward bias *EL*2 is fully occupied. Thus

$$n_t|_{\mathrm{for}} = N_t^n \ . \tag{1}$$

On the other hand, the occupancy of the levels in the depleted region created by reversed bias is only partial, since it is determined by the balance between electron photoionization transitions to the conduction-band and hole photoionization transitions to the valence band:

$$n_t|_{\mathrm{rev}} = N_t^n(1+\sigma_n^I/\sigma_p^I)^{-1} \ . \tag{2}$$

The difference in transition rates by a factor of 2 corresponds to $\sigma_p^I \simeq \sigma_n^I$, which leads to $n_t|_{\mathrm{rev}} = \frac{1}{2}N_t^n = \frac{1}{2}n_t|_{\mathrm{for}}$.

The above results provide the first experimental proof of the effect of *EL*2 occupancy on the transition rate to the metastable state. They also verify the validity of the assumption that the transition originates in the occupied *EL*2. Such an assumption, although commonly made, has never before been directly verified.

The dependence of the transition rate ($dC_2/dt|_{t\to 0}$) on photon energy is shown in Fig. 3, together with the no-phonon line of the *EL*2 intracenter absorption.[17] Due to the very low illumination density necessary for high spectral resolution, the transients $\Delta C_2(t)$ were extremely slow, with a time constant τ^* of the order of 10–100 h. Thus, the transition line rate was determined from high-sensitivity differential measurements of $\Delta C_2/\Delta t$ rather than from the total capacitance transient $C_2(t)$.

It is clearly seen in Fig. 3 that the spectrum of the transition rate reveals a very narrow peak, within an energy range of about 5 meV. The position of this peak agrees very well with that of the no-phonon line of optical absorption. The larger width of the photocapacitance peak is due to the larger spectral slit width used in this experiment. The no-phonon line has been identified as an As antisite intracenter transition from the ground state $^1A_1$ to the $^1T_2$ excited state.[18,19] These states were also theoretically predicted to be associated with occupied (neutral) As antisites. Thus, these results provide further strong evidence that in the transition to the metastable state a neutral As antisite defect is involved. This transition originates in the $^1A_1$ ground state and is finalized via the $^1T_2$ excited state.

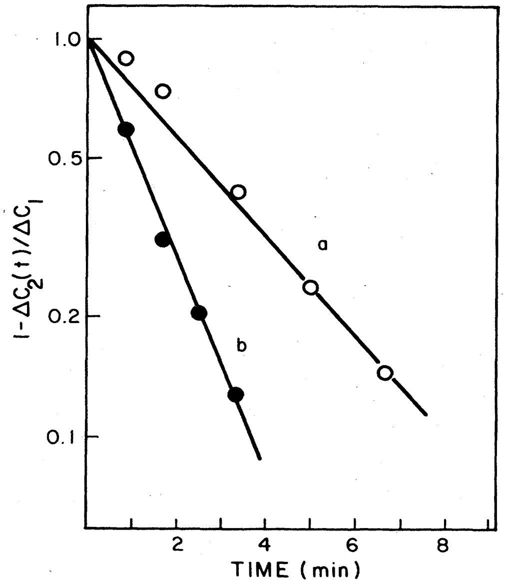

FIG. 2. Depedence of $N_t^*/N_t \simeq 1-\Delta C_2(t)/\Delta C_1$ on illumination time for curve *a* diode under reverse bias during illumination, and curve *b* diode under forward bias. Measurement done at 8 K; photon energy $h\nu = 1.18$ eV.

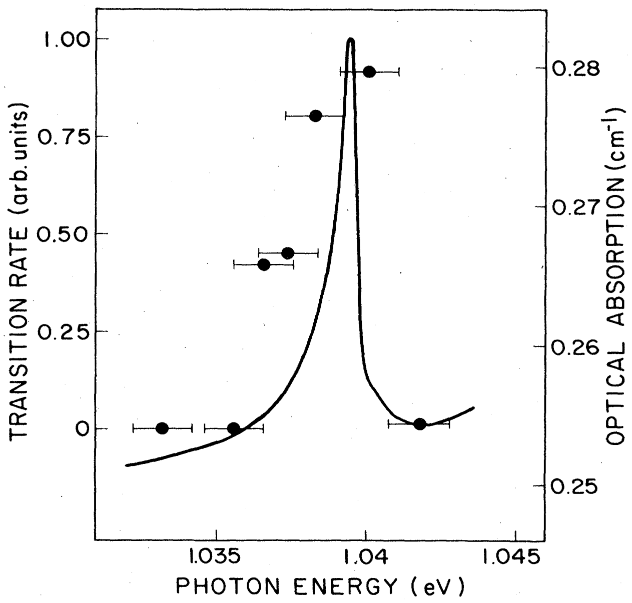

FIG. 3. High-resolution spectrum of the transition rate to the metastable state of *EL*2 (points) and corresponding no-phonon absorption line of *EL*2 intracenter transition (solid line). Measurements done at 8 K.

In view of the above results, the rate of the transition from the normal to the metastable state $R_{n\to m}=-dN_t^n/dt$ can be expressed (for low temperatures where thermal recovery is negligible) as

$$R_{n\to m}=n_t^{\mathrm{exc}}r_2\ , \tag{3}$$

where n_t^{exc} is the occupation of the $^1T_2$ excited state, and r_2 is the transition rate from the excited to the metastable state.

The balance between the intracenter-recombination transitions yields $n_t^{\mathrm{exc}}=I\sigma_{\mathrm{IC}}n_t/r_1$, and thus

$$R_{n\to m}=I\sigma_{\mathrm{IC}}n_t r_2/r_1\ , \tag{4}$$

where I is the photon flux, σ_{IC} is the optical cross section for intracenter transitions, and r_1 is the recombination rate for intracenter transitions from the excited to the ground level of the normal state.

As pointed out above, n_t has different values for reverse and forward bias. Expression (4) combined with (1) and (2) account very well for the characteristics revealed in the present experiments. Thus, the enhancement of $R_{n\to m}$ upon application of a forward bias is associated with an increase in $EL2$ occupation (n_t). The fine structure identified in the excitation spectrum $R_{n\to m}$, which is very similar to that of the no-phonon line of the intracenter absorption, is due to the optical cross section σ_{IC} (which is proportional to optical absorption). Finally, the low values of the overall transition rate $R_{n\to m}$ (which are about two orders of magnitude lower than $EL2$ photoionization rates and the rates of the intracenter transitions) can be explained as being due to the very different intracenter recombination, i.e., $r_1 \gg I\sigma_{\mathrm{IC}}$ and $r_1 \gg r_2$. Upon rewriting Eq. (4) in the form

$$\frac{dN_t^n}{dt}=-\frac{N_t^n}{\tau^*}\ , \tag{5}$$

it becomes apparent that the time constant $\tau^*=r_1N_t^n/r_2I\sigma_{\mathrm{IC}}n_t$, which explains the very large values of τ^*, which are much larger than $(I\sigma_{\mathrm{IC}})^{-1}$, and thus also much larger than $[I(\sigma_n^I+\sigma_p^I)]^{-1}$.

The present findings have important implications in the formulation of microscopic models of the $EL2$ metastability. Thus, the fact that metastability is induced by intracenter transitions (and not by photoionization) rules out the model of structural relaxation which is controlled by the charge state of defects forming the $EL2$ center as proposed in Ref. 20. In fact, the charge state of $EL2$ does not change during the transition to the metastable state.

The presence of the no-phonon line in the excitation spectrum is a strong argument against a complex involving nearest neighbors (such as $\mathrm{As_{Ga}}$ plus arsenic and gallium vacancies).[21,22] Defects located on the nearest lattice sites would change the tetrahedral symmetry of the antisite defect revealed by the no-phonon line. The photoexcitation of the isolated and electrically neutral arsenic antisite would be a preferable choice for a microscopic model of metastability. However, the large lattice relaxation cannot be readily explained in terms of the simple breathing distortion of the nearest neighbors.[23] Perhaps redistribution of bound electrons[24] and coupling with other asymmetric relaxation modes must be considered.

The present finding that the transition of $EL2$ to a metastable state originates in the electrically neutral state of $\mathrm{As_{Ga}}$ has serious bearing on the interpretation of photoquenching effects, especially those studied by magnetic resonance techniques, i.e., EPR (Refs. 4 and 25) and electron-nuclear double resonance (ENDOR).[3,26] These techniques detect the singly ionized state $\mathrm{As_{Ga}^+}$, which is paramagnetic and not the neutral state of $\mathrm{As_{Ga}}$. This ionized state does not directly participate in the transition to the metastable state. It is thus apparent that the photoquenching characteristics of EPR and ENDOR signals originating from $\mathrm{As_{Ga}^+}$ must be different from the photoquenching characteristics of $EL2$ as revealed by capacitance transients or intracenter optical absorption in which a neutral $\mathrm{As_{Ga}}$ defect is involved. Actually, recent results on the photoquenching characteristics of $\mathrm{As_{Ga}^+}$-related ENDOR signal have indeed been found to be different than those of intracenter absorption.[3] These differences indicated that $EL2$ is not an isolated $\mathrm{As_{Ga}}$ defect, as it was not realized that the photoquenching involves a neutral $\mathrm{As_{Ga}}$ defect.

In summary, kinetics studies of the $EL2$ transition to its metastable state employing capacitance transients and high-resolution optical absorption have shown that the rate of the transition increases as the occupancy of $EL2$ increases, and that this transition is associated with an intracenter transition in the neutral As antisite defect.

Note added in proof. An independent observation of the 1.039 eV no-phonon line in the excitation spectrum of $EL2$ transition to a metastable state has been recently reported by W. Kuszko and M. Kaminska at the Fifth Conference on Deep Impurity Centers in Semiconductors, St. Andrews, Scotland, June, 1985 (unpublished). Their study, however, employed bleaching of optical absorption and not the photocapacitance method.

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